

## MASS SPECTROMETRIC STUDIES OF THE CHEMICAL COMPOSITION OF COAL TARS PRODUCED IN A LAMINAR FLOW REACTOR

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### ABSTRACT

Curie-point desorption in combination with Gas Chromatography/Mass Spectrometry (GC/MS) and, alternatively, with direct Low Voltage Mass Spectrometry (LV-MS) was used to investigate the chemical composition and structure of condensed tar vapors produced during rapid devolatilization (heating rate  $\sim 10,000$  K/sec) of carefully sized coal particles representing the Beulah Zap, Big Blue, Illinois #6, Pittsburgh #8, and Pocahontas #3 seams, respectively, using the laminar flow reactor described by Fletcher et al [1], at two gas temperatures (1050 K and 1250 K).

Tar samples were collected by means of a special probe [1] at different points downstream of and corresponding to residence times between 70 and 250 msec. GC/MS analyses of the corresponding tars indicate that the degree of aromaticity increased rapidly as a function of residence time at the 1250 K gas temperature condition. Moreover, at 1250 K devolatilization is complete within 70 msec and beginning secondary gas phase reactions of tar vapors (viz. marked increases in PNAH content and corresponding decreases in phenolic components) are observed within less than 100 msec. However, at 1050 K the coal devolatilization process appears to be barely complete after 250 msec and little or no evidence of secondary gas phase reactions is found.

### INTRODUCTION

Recent devolatilization studies [1-5] have identified the rates and the temperature regimes of pulverized coal devolatilization as a function of heating rate, final temperature, and coal type. Careful particle temperature measurements during devolatilization at rapid heating conditions [1-2] have eliminated many uncertainties caused by estimations of particle temperatures in early studies.

Current devolatilization models have advanced beyond one-step Arrhenius kinetics to descriptions of the bonding structure in the coal, metaplast, and tar [6-9]. Other models include detailed empirical correlations to estimate yields of tar products from elemental compositions of the parent coal [10], as well as mechanism to describe the evolution of the physical structure of char particles [11]. Most of these models presume a mechanism for generation of metaplast during pyrolysis, followed by release of lighter fractions of the metaplast as tar vapor, where tar is commonly defined as pyrolysis products that condense at room temperature and pressure. It is clear that quantitative experimental investigations of the evolution of the chemical structure of solid and condensable pyrolysis products (char and tar) are critical to the understanding of coal devolatilization mechanisms.

The present study addresses the characterization of condensable tar vapors, produced by rapid ( $\sim 10^4$  K/sec) heating of pulverized coals in a laminar flow reactor. Curie-point desorption GC/MS and

direct Low Voltage MS methods were used to characterize tar samples at the molecular level and to elucidate some of the underlying reaction mechanisms.

## EXPERIMENTAL

### Reactor and Sample Collection System:

Experimental details regarding the particle temperature measurements and sample collection system were previously published [1], and hence only a brief discussion will be given here. The pyrolysis studies were performed in 100% nitrogen in a laminar flow reactor [1]. Transparent (quartz glass) flow reactor walls allow radiant emission from the coal particles to be monitored at any axial location. Two gas temperature conditions were used in this study, with maximum centerline gas temperatures of 1050 and 1250 K.

An infrared sizing pyrometer system was used to measure size, temperature, and velocity of individual particles in the flow reactor at different axial locations. Typical standard deviations in measured particle temperatures are 5 K for pure carbon spheres (Spherocharb) and 30 K for coal particles. A water-cooled, helium-quench probe was used to collect solid samples iso-kinetically. A virtual impactor and three-stage Andersen cyclone system were used to aerodynamically separate char particles from condensed tar vapors and aerosols. Tars were collected on polycarbonate filters following the separation system [1].

Collected tars were shipped overnight to the analytical facility frozen in an ice chest and stored at -90 C. Five milligrams of the tar samples were suspended in 1 ml of Spectrograde methanol and the homogeneity of each suspension enhanced with a vibrating mixer.

### Curie-Point GC/MS and Low Voltage MS Analyses:

GC/MS analyses of the tar samples were performed using a Hewlett-Packard 5890 chromatograph with a 15 m x 0.25 mm i.d. x 0.25  $\mu$ m film thickness DB-5 column (J&W Scientific). The conditions used in GC/MS were as follows: electron energy 70 eV, Ion Trap Detector (ITD, Finnigan MAT) scanned from m/z 40-450 at 1 scan/sec, pyrolysis time 2 sec, 610 C Curie-point wires in an inlet set at 250 C. The column was temperature programmed from 40-300 C at 15 C/min.

LV-MS experiments were carried out using an Extranuclear Model 5000-1 Curie-point pyrolysis MS system. Twenty five microgram quantities of tar sample were coated on ferromagnetic wires from methanol suspensions. The wires were inserted into borosilicate glass reaction tubes and introduced into the vacuum system of the mass spectrometer. The ferromagnetic wires were inductively heated at approx. 100 C/s to an equilibrium temperature of 610 C. Total heating time was 10 s. LV-MS conditions were as follows: electron ionization at 12 eV (set value), scanning rate 1000 amu/s, total scanning time 20 s, mass range scanned m/z 40-260.

## RESULTS AND DISCUSSION

Low Voltage mass spectra of tars obtained by Curie-point desorption directly in front of the ion source and representing two different coals are shown in Figure 1a-e. Comparison of the Bucalah Zap tar sample produced at 1250 K and collected after 70 msec with the corresponding 250 msec sample shows major changes characterized by a marked decrease in hydroxyaromatic signals (e.g., alkylsubstituted phenols, dihydroxybenzenes and naphthalenes) accompanied by a strong increase in polycondensed aromatic hydrocarbons, e.g., phenanthrenes and pyrenes, in the 250 msec sample. Apparently, this marked change is due to secondary reactions. Especially the dominance of unsubstituted

pyrene among the various alkylsubstituted homologs is a telltale sign of high temperature gas phase reactions and may perhaps be seen as a first step in the direction of soot formation.

The Beulah Zap tar pattern at 70 msec, on the other hand, compares well with direct Curie-point pyrolysis mass spectra of North Dakota coal [12], indicating that at 70 msec primary pyrolysis products (e.g., dihydroxybenzenes) still dominate, although the yield of polycondensed aromatic hydrocarbons e.g., (alkyl) phenanthrenes, is already higher than would be observed under vacuum micropyrolysis conditions. The tar patterns of Pittsburgh #8 coal at 1250 K (Figures 1c and d) are in excellent agreement with these observations. Again the short residence time pattern (80 msec) corresponds quite well with the Curie-point pyrolysis mass spectrum, e.g. as reported by Chakravarty et al. [13], whereas the long residence time (250 msec) tar shows a pronounced shift towards polycondensed aromatic hydrocarbon. Due to the higher rank (hvAb) of the Pittsburgh #8 coal, however, the short residence time spectrum (Figure 1c) is clearly different from that of the Beulah Zap lignite, e.g., with regard to the lower (alkyl) dihydroxybenzene intensities and increased (alkyl) naphthalene series. This is in agreement with trends observed in earlier Py-MS studies of coals of different rank [14].

Finally, the effect of temperature is briefly illustrated in Figure 1e (Pittsburgh #8, 1050 K). In spite of the long residence time (250 msec) the MS pattern in Figure 1e is highly similar to that in Figure 1c, indicating the absence of marked secondary reactions at this lower temperature.

The usefulness of Curie-point desorption GC/MS techniques for confirming and further elucidating the above discussed trends and effects is illustrated in Figures 2 and 3. Illinois #6 tars produced at 1250 K and collected after 70 msec (Figure 2) and 250 msec (Figure 3), respectively, show an approx. 100 X reduction in the relative abundance of (alkyl) phenols accompanied by a 10 X increase in selected polycondensed (4-6 ring) aromatic hydrocarbons.

Although in the current experimental set-up absolute tar yields cannot yet be established with sufficient certainty to enable precise quantitative studies, e.g., for determining the kinetics of the gas phase condensation reactions, changes in the relative composition as a function of residence time are illustrated for Big Blue tars at 1050 K in Figure 4 and for Beulah Zap, Illinois #6 and Pittsburgh #8 tars in Figures 5a, b and c, respectively. At 1050 K fragment ions of aliphatic hydrocarbons (e.g., at  $m/z$  85, 57, 43, see Figure 4c) dominate the short residence time (120 msec) tar. Based on previous, time-resolved pyrolysis field ionization MS studies [15], early evolution of aliphatic hydrocarbon moieties during devolatilization of low rank coals is likely to represent the desorption of low MW biomarker type compounds, e.g., branched and/or alicyclic terpenoids. At 150 msec the relative intensities of the aliphatic hydrocarbon moieties are starting to decrease due to the strong increase in hydroxaromatics, e.g., dihydroxybenzenes at  $m/z$  110 and 124 (Figure 4b). Finally, at 250 msec, the relative abundance of compounds such as naphthols, are still increasing suggesting that the devolatilization process may not yet be fully completed. On the other hand, suspected secondary reaction products such as pyrenes and perylenes are starting to increase slightly. Nevertheless, the relative abundance of the highly reactive dihydroxybenzenes appears to be more or less stable. Altogether, our tentative conclusion is that at 1050 K the devolatilization process of Big Blue coal is close to being complete after 250 msec.

A drastically different picture is obtained at 1250 K, as illustrated for the three coals in Figure 5. Compounds such as pyrenes, perylenes and even picenes appear to be increasing right from the start, whereas the relative abundances of naphthols and even phenanthrenes are decreasing after approx. 100-150 msec., suggesting the occurrence of marked secondary gas phase reactions. Unfortunately, at the time of writing no tar samples had been produced at intermediate temperatures, e.g., 1150 K. If the above observations at 1050 and 1250 K are correctly interpreted, devolatilization at 1150 K should be completed within 100-200 msec and the onset of secondary gas phase reactions should become clearly visible at longer residence times.

## CONCLUSIONS

Based on the Curie-point GC/MS and Low Voltage MS analyses of the tar formed during devolatilization of Beulah Zap, Big Blue, Illinois #6, Pittsburgh #8, and Pocahontas #3 coals, the following conclusions are reached:

1. The degree of aromaticity increases rapidly as a function of residence time at the 1250 K gas temperature.
2. However, little increase in aromaticity can be detected at the 1050 K gas temperature.
3. At a gas temperature of 1250 K devolatilization is complete within 70 msec and secondary gas phase reactions of tar vapors can be observed within 100 msec.
4. At 1050 K, the devolatilization process appears to be more or less complete after 250 msec.
5. In order to study complete devolatilization process and the possible onset of secondary reactions, further experiments should be conducted at an intermediate temperature, e.g., 1150 K.

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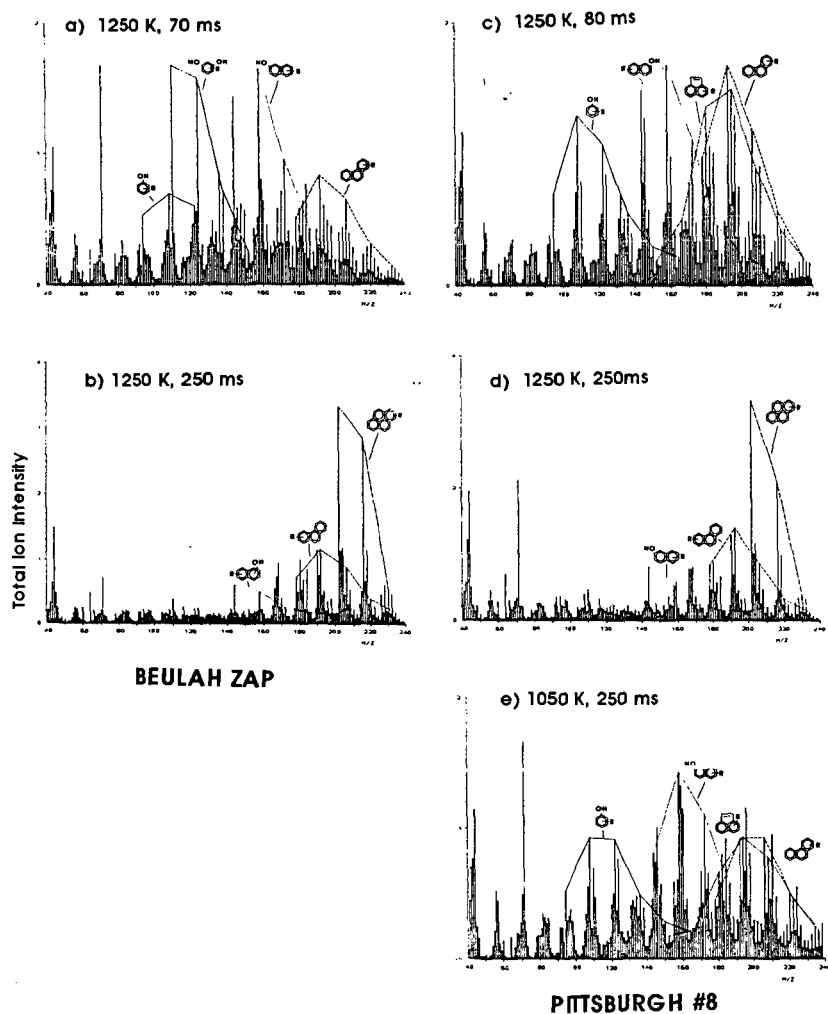


Figure 1. Curie-point desorption mass spectra of Beulah Zap and Pittsburgh #8 tars showing the effects of coal rank (a and b vs. c, d and e), residence time (a and c vs. b, d and e) and gas temperature (e vs. a, b, c and d).

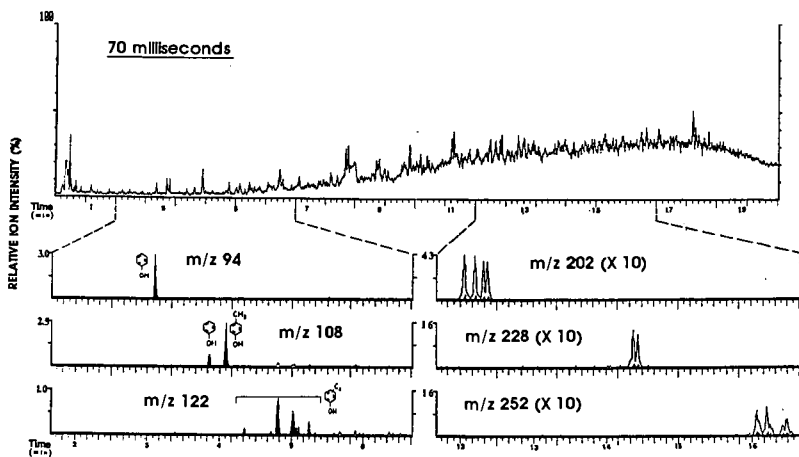


Figure 2. Curie-point desorption GC/MS profiles of Illinois #6 tar obtained at 1250 K after 70 msec. Total ion chromatogram (upper profile) and selected ion chromatograms (lower profiles) show relative abundance of (alkyl) phenols vs. pyrenes, perylenes and picones.

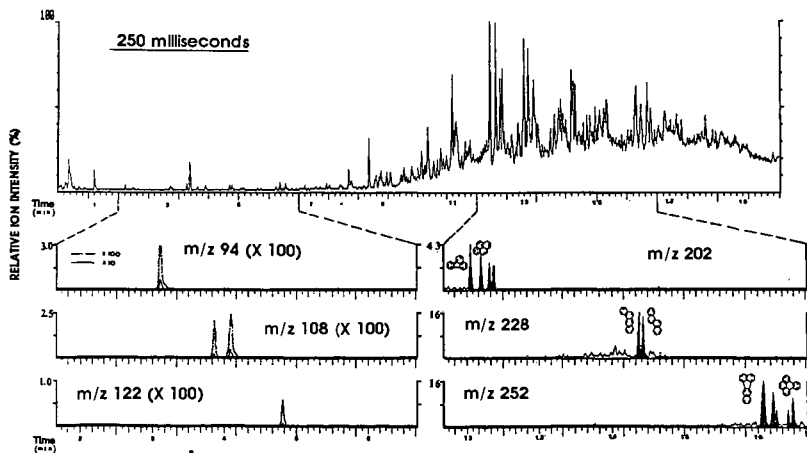


Figure 3. As Figure 2 but obtained after 250 msec. Note 100-fold decrease in (alkyl) phenol as opposed to 10-fold increase in polynuclear aromatic hydrocarbons.

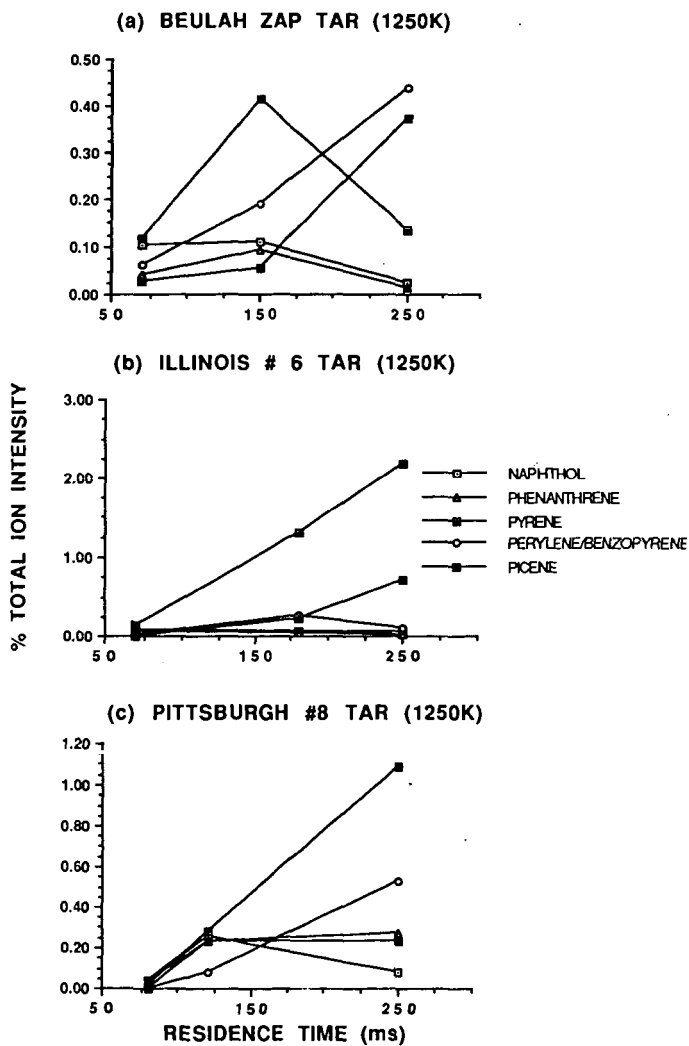


Figure 5. As Figure 4 but representing tars from 3 different coals obtained at 1250 K.

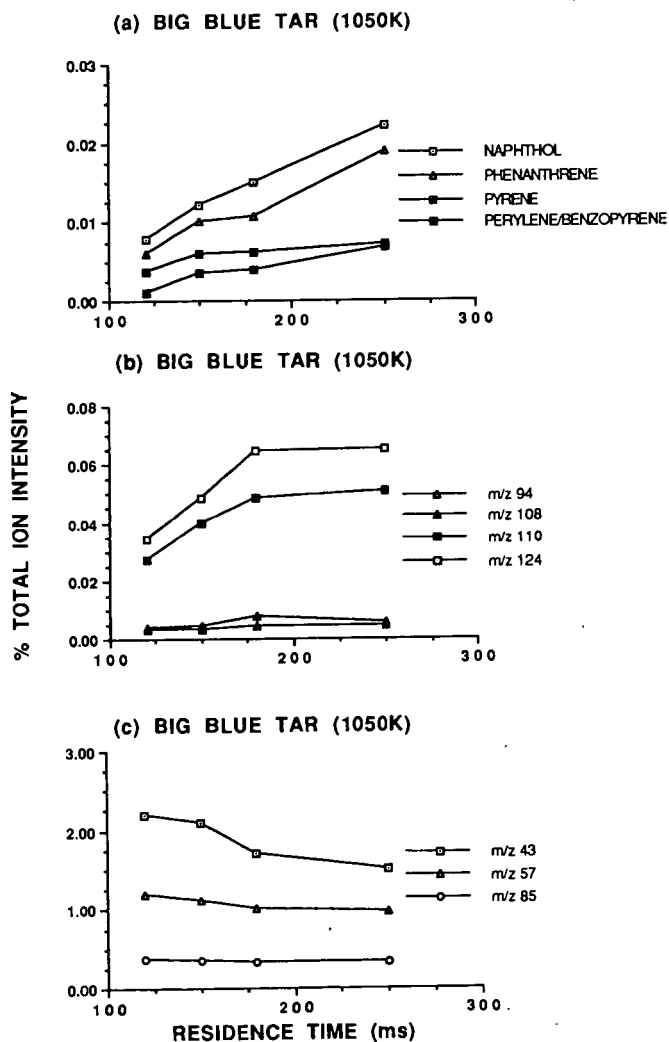


Figure 4. Relative abundance of selected ion profiles in Curie-point desorption GC/MS data on Big Blue tar samples obtained at 1050 K and at different residence times.